

*B. B. Mahapatra & S. K. Panda*

Biokemistri  
Vol. 22, No. 2, December 31, 2010  
Printed in Nigeria

0795-8080/2010 \$12.00 + 0.00  
© 2010 Klobex Academic Publishers  
<http://www.klobex.org/bkr>  
Also available online at <http://www.bioline.org.br/bk>

BKR 2010137/22201

## Coordination Compounds of $\text{Co}^{\text{II}}$ , $\text{Ni}^{\text{II}}$ , $\text{Cu}^{\text{II}}$ , $\text{Zn}^{\text{II}}$ , $\text{Cd}^{\text{II}}$ and $\text{Hg}^{\text{II}}$ with Tridentate ONS Donor Azo dye Ligands.

Bipin B. Mahapatra\* and Saroj Ku. Panda \*\*

\*\*P.G. Department of Chemistry, G.M. (Autonomous) College, Sambalpur – 768004 (Orissa). India

Telephone No : - 06632401177

E-mail: [mahapatra.bipin@yahoo.com](mailto:mahapatra.bipin@yahoo.com) \*, [sarojbadmal@gmail.com](mailto:sarojbadmal@gmail.com) \*\*

(Received September 7, 2010; Accepted December 10, 2010)

**ABSTRACT** : Twelve monomeric co-ordination compounds of  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  with two ONS tridentate azodye ligands have been synthesized. The characterizations of these compounds have been made basing upon analytical conductance, magnetic susceptibility, I.R, electronic spectra, E.S.R. and N.M.R. spectral data. The  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes are found to be octahedral,  $\text{Cu}^{\text{II}}$  complexes are distorted octahedral and  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  and  $\text{Hg}^{\text{II}}$  complexes are found to be four co-ordinated possibly with tetrahedral geometry.

**Key words:** Azodye complexes, Co-ordination compounds, Metal complexes.

### Introduction

The synthesis of co-ordination compounds using polydentate azodyes as ligands is of recent interest. Besides laboratory and industrial applications, the chemotherapeutic use<sup>1</sup> (Gaind *et al*, 1964) of azodyes has inspired the modern chemists to prepare new metal chelates by reacting with new polydentate azodyes with different transitional and non-transitional metal ions, in order to study their pharmacological properties. In continuation of our earlier work<sup>2</sup> (Mahapatra *et al* 2009), the present paper describes the preparation of two new oxygen, nitrogen and sulphur donor tridentate azodye ligands (Figs. 1 & 2) and their twelve monomeric co-ordination compounds.

### Materials and Methods

All the chemicals were of B.D.H. or E. Merck grade. Metal, carbon, hydrogen, nitrogen and chlorine were estimated by standard methods<sup>3</sup> (Vogel, 1969). Conductivity measurement in DMF was made using Toshniwal CL 01-06 Conductivity bridge. Magnetic moment was measured at RT by Gouy method. I.R. Spectra (KBr) were recorded on an IFS 66U Spectrophotometer, electronic spectra ( $10^{-2}\text{M}$  in acetone) using Hilger-Watt uvispeck spectrophotometer, N.M.R. spectra on a Jeol GSX 400 with acetone- $d_6$  as solvent and TMS as internal standard and ESR spectra on an  $\text{E}_4$ - spectrometer.

---

\*\*To whom correspondence should be addressed.

### Preparation of the ligand:

#### Preparation of ammonium phenyldithiocarbamate

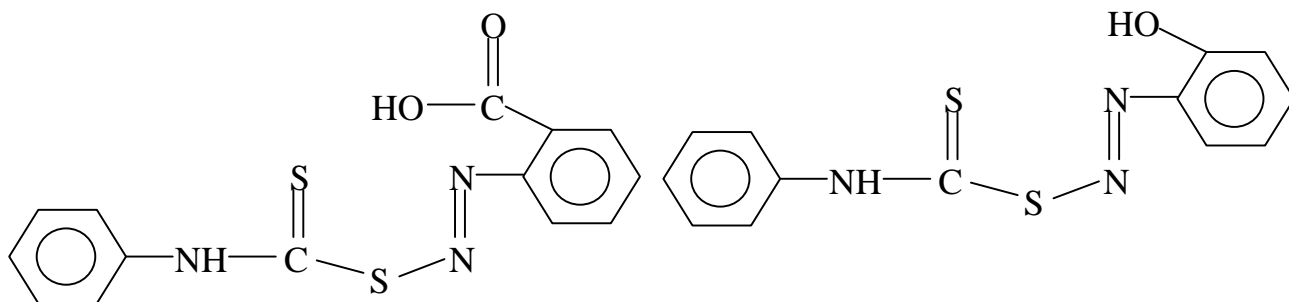
Conc. ammonium hydroxide (8.5 ml) was added slowly to distilled aniline (9.13 ml) at 0 – 5°C in an ice salt freezing mixture. Then distilled carbon disulphide (6.0 ml) was added drop wise with constant stirring for 1 hour with the help of a mechanical stirrer. The resulting white crystalline solid was obtained with decomposition temperature 33 - 35°C. It was dried on exposure to air.

#### Preparation of o-hydroxy/o-carboxyphenylazophenyldithiocarbamate :-

To a cold solution of freshly prepared ammoniumphenyldithiocarbamate ( 9.3 gm in 100 ml), a cold aqueous solution of equimolecular amount of the diazonium chlorides obtained from O-aminophenol/O-aminobenzoic acid was added drop wise with stirring. The resulting solid compounds of reddish brown azodyes were obtained. These were then washed with distilled water, dried and crystallized from absolute ethanol.

#### Preparation of the complexes :-

The metal chlorides in ethanol were mixed separately with the ligands in dioxane in 1:1 molar ratio. The resulting solutions were heated to ~60 – 70°C for about 1 hour in a heating mantle. On cooling the P<sup>H</sup> of the solutions were raised to ~7. The solid complexes thus separated were then washed with ethanol followed by ether and then dried in vacuum.

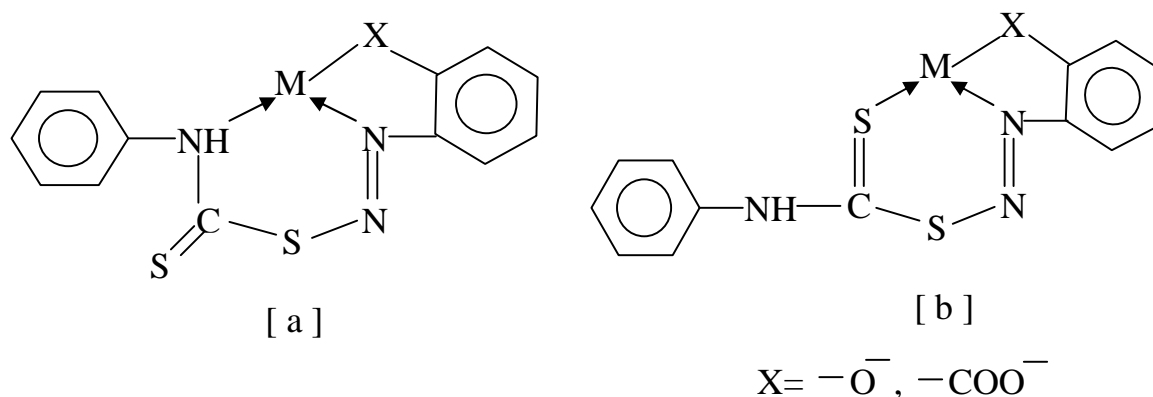


[ Fig-1 ]

[ Fig-2 ]

### Results and Discussion

The co-ordination compounds synthesized have the compositions  $[M(L/L^1)Cl(H_2O)_2]$ ,  $[M^1(L/L^1)Cl]$  where  $M = Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$ ;  $M^1 = Zn^{II}$ ,  $Cd^{II}$ ,  $Hg^{II}$ ;  $LH = o$ -carboxyphenylazophenyldithiocarbamate ( $C_{14}H_{11}N_2OS_2$ ) (Fig 1)  $L^1H = o$ -hydroxyphenylazophenyldithiocarbamate. ( $C_{13}H_{11}N_2OS_2$ ) (Fig 2). All the complexes are either crystalline or amorphous in nature, and soluble in common organic solvents. The non-electrolyte nature of the complexes in DMF is shown from the low conductance values ( $4.2 - 5.6 \Omega^{-1} cm^2 mol^{-2}$ ). Both the ligands can be represented by two possible structure 3(a) and 3(b). In structure 3(a) the secondary nitrogen atom is bonded to the metal ions and in structure 3(b) the bonding of thione sulphur to the metal ions is observed.



[Fig. 3 ]

In the i.r. spectra of the ligands, the bands are obtained at  $3298.9\text{cm}^{-1}$  (LH) and  $3206.5\text{cm}^{-1}$  (L'H) which may be ascribed to intramolecular O-H...N hydrogen bonding. Disappearance of these bands in the metal chelates indicates the bonding of phenolic and carboxyl oxygen atoms to the metal ions. In the ligand (LH)  $\nu_{\text{as}}$  ( $\text{COO}^-$ ) and  $\nu_{\text{s}}$  ( $\text{COO}^-$ ) bands appear at  $1633.8\text{cm}^{-1}$  and  $1438.9\text{cm}^{-1}$  respectively and these bands appear in the metal chelates at  $\sim 1589.8\text{cm}^{-1}$  and  $\sim 1402.5\text{cm}^{-1}$  with a difference  $\Delta\nu$  of  $\sim 187.3\text{cm}^{-1}$  supporting monodentate nature of the carboxylate group<sup>4</sup>(Deccan & Philip 1980). The band at  $1494.8\text{cm}^{-1}$  (L'H) can be assign to phenolic C- O vibration and in the metal chelates this band appears at  $\sim 1467.7\text{cm}^{-1}$  indicating the bonding of the ligand to the metal ions through phenolic oxygen atom<sup>5</sup>(Mishra & Keshri 1981).The sharp band observed at  $1592.7\text{cm}^{-1}$  (LH) and  $1592.9\text{cm}^{-1}$  (L'H) can be attributed to  $\nu_{(-\text{N}=\text{N}-)}$  vibration and in the metal complexes these bands appear at  $\sim 1548.2\text{cm}^{-1}$  and  $\sim 1594.7\text{cm}^{-1}$  respectively which indicates the bonding of one of the the azo nitrogen atoms to the metal ions<sup>6</sup>(King R. B 1966). In the ligands sharp bands are observed at  $1038.0\text{cm}^{-1}$  (LH) and  $1070.9\text{cm}^{-1}$  (L'H) which can be attributed to  $\nu(\text{C}=\text{S})$  vibration and in the metal complexes this band is observed at  $1019.4\text{cm}^{-1}$  and  $1023.5\text{cm}^{-1}$  respectively which indicates the bonding of thiocarbonyl sulphur atom to the metal atoms<sup>7</sup>(Namakato & fujita 1963). in the metal chelates broad bands appear at  $\sim 3319.1\text{-}3550.9\text{cm}^{-1}$  and  $\sim 840.2\text{cm}^{-1}$  followed by sharp peaks at  $730.1\text{-}725.4\text{cm}^{-1}$  assignable to-OH stretching, rocking and wagging vibrations respectively indicating the presence of co-ordinated water molecules in the complexes<sup>8</sup>(Namakato 1963). The conclusive evidence of bonding of the ligands to the metal ions is proved by the appearance of bands at  $515.8\text{cm}^{-1}$ -  $498.9\text{cm}^{-1}$  assigned to (M-O) and  $420.1\text{-}421.6\text{cm}^{-1}$  (M - N)<sup>9</sup>(Ferraro 1971).

In the electronic spectra of  $\text{Ni}^{\text{II}}$  complexes, four ligand field bands are observed at 10232(10256), 17552(17685) 25180(25250) and 32445(32525)  $\text{cm}^{-1}$  assignable to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  $\rightarrow {}^3\text{T}_{1g}(\text{F})$  ( $\nu_2$ ),  $\rightarrow {}^3\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) and CT transition respectively in an octahedral geometry. The ligand field parameters like  $\text{Dq} = 732.000(742.900)\text{cm}^{-1}$ ,  $\text{B} = 802.400(811.133) \text{ cm}^{-1}$ ,  $\beta_{35} = 0.826(0.835) \text{ cm}^{-1}$ ,  $\nu_2/\nu_1 = 1.715(1.724)$  and  $\sigma = 21.065\%$  (19.760%) also support the octahedral symmetry for the complexes<sup>10</sup>(Sacconi 1968). In the electronic spectra of the  $\text{Co}^{\text{II}}$  complexes four ligand field bands are observed at 8250(8235), 16575(16510), 20342(20452) and 32150(32355)  $\text{cm}^{-1}$ . The first three bands can be attributed to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  $\rightarrow {}^4\text{A}_{2g}(\text{F})$  ( $\nu_2$ ) and  $\rightarrow {}^4\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) transitions respectively and the fourth band is assigned to a CT band. The ligand field parameters like  $\text{Dq} = 832.500(827.500) \text{ cm}^{-1}$ ,  $\text{B} = 811.133(817.133) \text{ cm}^{-1}$ ,  $\beta_{35} = 0.835(0.841) \text{ cm}^{-1}$ ,  $\nu_2/\nu_1 = 2.009(2.005)$  and  $\sigma = 19.760\%$  (18.906%) suggest an octahedral geometry for the complexes<sup>11</sup>(Lever 1967). The electronic spectra of  $\text{Cu}^{\text{II}}$  complexes show one broad band at  $\sim 13375\text{--}14450 \text{ cm}^{-1}$  with maxima at  $\sim 14310 \text{ cm}^{-1}$  assignable to  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition in support of a distorted-octahedral configuration of the complexes<sup>12</sup>(Yamada 1966).

The  $^1\text{H}$  NMR spectra of the ligands (LH) and ( $\text{L}^1\text{H}$ ) were recorded in acetone- $d_6$ . The complex pattern observed at  $\delta$  6.9300–8.3028 (LH) and  $\delta$  6.9047–8.2739 ( $\text{L}^1\text{H}$ ) corresponds to 09 phenyl protons each. The  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  complexes exhibit magnetic moments at  $\sim 5.0$ ,  $\sim 3.1$  and  $\sim 1.8$  B.M. indicating the presence of three, two and one unpaired electron respectively<sup>13</sup> (Cotton & Wilkinson, 1985).

The 'g<sub>av</sub>' values of the complexes [CuLCl(H<sub>2</sub>O)<sub>2</sub>] and [CuL<sup>I</sup>Cl (H<sub>2</sub>O)<sub>2</sub>] were found to be 2.0979 and 2.0441 respectively by Kneubuhl's method<sup>14</sup>(Kneubuhl, 1966). This type of spectra may be due to dynamic or pseudo rotational behaviour of Jahn-Teller distortion. The covalent nature of the Cu–L band is indicated from low 'g<sub>av</sub>' value (< 2.3). This value is consistent with Cu–O and Cu–N bonded copper complexes.

The Zn<sup>II</sup>, Cd<sup>II</sup> and Hg<sup>II</sup> complexes are suggested to be four-coordinated probably with tetrahedral geometry basing upon analytical, conductance and i.r spectral data.

Hence both the azodyes behave as tridentate ligands being bonded through azo nitrogen, phenolic or carboxylic oxygen and thione sulphur atoms.

Table-1 Analytical and Physical data of the complexes:

Compound	Colour	%Metal Found (Calculated)	%Nitrogen Found (Calculated)	%Sulphur Found (Calculated)	μ <sub>eff</sub> B.M.
LH (C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> S <sub>2</sub> O <sub>2</sub> )	Reddish brown	-	9.1 (9.24)	20.9 (21.12)	-
L <sup>I</sup> H (C <sub>13</sub> H <sub>11</sub> N <sub>2</sub> S <sub>2</sub> O)	Reddish brown	-	9.9 (10.18)	23.1 (23.27)	-
[CoLCl (H <sub>2</sub> O) <sub>2</sub> ]	Violet	13.5 (13.63)	6.3 (6.47)	14.7 (14.80)	5.0
[CoL <sup>I</sup> Cl (H <sub>2</sub> O) <sub>2</sub> ]	Brown	14.4 (14.57)	6.8 (6.92)	15.7 (15.82)	5.1
[NiLCl (H <sub>2</sub> O) <sub>2</sub> ]	Brown	13.4 (13.57)	6.3 (6.48)	14.7 (14.81)	3.1
[NiL <sup>I</sup> Cl (H <sub>2</sub> O) <sub>2</sub> ]	Reddish brown	14.3 (14.51)	6.8 (6.93)	15.7 (15.83)	3.0
[CuLCl (H <sub>2</sub> O) <sub>2</sub> ]	Coffee colour	14.4 (14.53)	6.2 (6.40)	14.5 (14.64)	1.8
[CuL <sup>I</sup> Cl (H <sub>2</sub> O) <sub>2</sub> ]	Brown	15.4 (15.53)	6.7 (6.84)	15.5 (15.64)	1.8
[ZnLCl]	White	16.0 (16.23)	6.8 (6.95)	15.7 (15.89)	-
[ZnL <sup>I</sup> Cl]	Brownish white	17.3 (17.44)	7.3 (7.47)	16.9 (17.07)	-
[CdLCl]	white	24.8 (24.99)	6.0 (6.22)	14.1 (14.23)	-
[CdL <sup>I</sup> Cl]	White	26.5 (26.64)	6.5 (6.63)	14.9 (15.17)	-
[HgLCl]	Grey	37.1 (37.28)	5.0 (5.20)	11.7 (11.89)	-
[HgL <sup>I</sup> Cl]	Brown	39.1 (39.32)	5.3 (5.49)	12.4 (12.54)	-

ACKNOWLEDGEMENT: The authors are thankful to the Head, SAIF, I.I.T. Madras for providing I.R., N.M.R. and E.S.R. spectral data.

## References

1. Gaind K.N and Khanna J.M: *Indian J. Pharm* **26**, pp.34-38, 1964. Goodman L.S. and Gilman A: "*The Pharmacological basis of Therapeutics*". 4<sup>th</sup> Ed<sup>n</sup>, Mc. Millan, New York, P-III, 1970.
2. Mahapatra B.B. and Sarangi A. K: *J. Indian Chem. Soc* **86**: pp. 559-563. 2009. Mahapatra B.B. and Patel N: *J. Indian Chem. Soc* **86**: pp. 518-523 2009. Mahapatra B.B. and Patel N: *Bangladesh Journal of Scientific and Industrial Research* 44(4): pp. 445 – 452. 2009.
3. Vogel A.I: *Text Book of Quantitative Analysis*. 3rd Ed<sup>n</sup>. Longman London. 1969.
4. Deccan G.B. and Phillips R.J: *Coord. Chem. Rev* 33, pp. 227-231, 1980. Bellamy L.J: "*The infrared spectra of complex molecules*", 3<sup>rd</sup> Ed<sup>n</sup>; Chapman and Hall, London. Nakamoto K: "*Infrared Spectra of Inorganic and Co-ordination Compounds*", 4<sup>th</sup> Ed<sup>n</sup> Wiley New York, pp. 230 – 233, 1986.
5. Mishra, L. K and Keshari, B. N: Thiohydrazides as complexing agent part 1 – complexes of Ni(II), Co(II & III), Cu(II), Zn(II), Cd(II), Pd(II) & Hg(II) with O – Hydroxyphenylthiohydrazide. *Indian J.Chem; Sect.A*, **28**: pp 883 - 887. 1981
6. King R.B and Bisnette M. B: Organonitrogen derivatives of Metal carbonyls. II. Aryl Azo derivatives of Molybdenum. *Inorg. Chem*, **5**, pp. 300-306, 1966.
7. Nakamoto K, Fujita T, Condrate R. A and Morimoto M: *J. Chem. Phys.*, **30**, pp.421-424, 1963.
8. Nakamoto. K: *Infrared Spectra of Inorganic and Co-ordination Compounds*. Wiley inter science New York: (1963)
9. Ferraro, J.R: *Low Frequency Vibration of Inorganic and Co-ordination Compound* Plenum press, New York USA: (1971).
10. Sacconi. L: *J. Inorg. Nucl. Chem.*, **18**, pp.73-77, 1968.
11. Lever A.B.P : "*inorganic electronic spectroscopy*". Elsevier, Asterdam, UK. Magree. R and Gordan. L: the infrastructure of chelate compounds – III : "*A study of some trivalent metal chelates compounds of 8-hydroxyquinoline in the region 5000-250cm<sup>-1</sup>*". *Talanta* .10 : pp. 967-970, 1963.
12. Yamada S: *Co-ord. Chem. Rev* 1 pp. 415-418, 1966. Proctor I. M, Halthway B. J and Nichol. P: *J.Chem.Soc(A)* pp.1678-1683, 1968,.
13. Cotton F.A. and Wilkinson P.G: *Advanced Inorganic Chemistry*. 3<sup>rd</sup> Ed<sup>n</sup>, Wiley- Eastern New Delhi. 1985.
14. Kneubuhl F.K: Approximation in calculation of EPR parameters. *J.chem.Phys.* **33**, pp. 1074-1078, 1960.